PROPERTIES OF HOT-PRESSED TaC-C & NbC-C COMPOSITES

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ABSTRACT

Tantalum carbide-graphite and niobium carbide-graphite composites have been prepared by hot-pressing at 3000° to 3200°C. The effect of metal carbide content upon properties such as flexural strength, thermal expansion, compressive deformation, and electrical resistivity have been determined, both parallel and perpendicular to grain direction. The results show that with increasing carbide content the following general trends are observed:

1) Higher strength
2) Decreasing anisotropy
3) Decreasing resistance to high temperature plastic deformation
4) Decreasing electrical resistivity

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I. INTRODUCTION

Metal carbides are the most refractory of all known materials and also exhibit high strength. Their use for high temperature applications has been limited by their susceptibility to thermal shock and also by difficulties in the machining of desired configurations. However, the incorporation of graphite to form a series of metal carbide-graphite composites has yielded materials which minimize the undesirable properties of pure carbides while exploiting their high strength.

Investigations conducted at IITRI have been concerned with the fabrication of such composites by hot pressing at temperatures of 2600° to 3250°C. No binders are used in this technique. Solid and/or liquid state sintering under pressure at these high temperatures is the mechanism by which the raw powder mixture is consolidated into a dense two-phase body.

The early studies have shown that addition of any of the carbides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, or tungsten to graphite result in strong, dense composites. Properties vary depending on the system and carbide content. The greatest potential for high temperature use has been shown by composites incorporating TaC or NbC. The carbide-carbon eutectic of these systems are reported as 3450°C[1] for TaC-C and 3220°C[2,3] for NbC-C. Somewhat lower minimum solidus temperatures are exhibited by HfC-C (3150°C)[3] and ZrC-C (2900°C).[3] This paper deals with mechanical properties of TaC-C and NbC-C at both room and high temperatures.

II. EXPERIMENTAL PROCEDURE

The various composites were fabricated by hot pressing binary mixtures of carbon and metal or metal-carbide at temperatures of 2900° to 3250°C. Calcined petroleum coke having

needle-like particles was used as the carbon source. The mean particle size of the metal powders was 15μ for Ta and 10μ for Nb. Carbide powders were somewhat finer, being of the order of about 3μ. The coke had an average particle size of about 15μ.

After dry blending for 16 hrs, the metal-carbon mixture was hot pressed, using induction heating in a 2½ in. ID CS graphite mold insulated with Thermax (Fig. 1). Initial pressure applied was 500 psi; this level was maintained until a temperature of 2000°C was attained at which time it was increased to 3000 psi for the remainder of the processing. Temperature readings were taken with an optical pyrometer (L & N brightness type) sighting into the mold through an argon purged sight tube. Using an 80 KW motor generator power source the processing temperature was reached in approximately 1 to 1½ hrs at which time the operation was concluded for most of the pressings.

In general, higher processing temperatures have been shown to be desirable. This is probably due to the increased diffusion occurring at higher temperatures which produces better bonding between the NbC and C and also to the higher degree of graphite orientation.

However, upper limits in temperature are defined. In the fabrication of NbC-C bodies, it has been found that exceeding the solidus (3220°C) results in a heterogeneous composite for graphite matrix materials. This appears in the form of a cone having its apex toward the top of the billet. As Fig. 2 shows, the cone area has a high density of carbide particles whereas the portion outside of the cone contains a lesser amount. The extruded material shows a eutectic structure indicating a temperature above 3220°C had been attained.

It is felt that this phenomenon is due to a combination of extrusion around the top punch and reaction with the mold wall of a mobile eutectic phase. The reason the cone has its base at the bottom graphite punch may be due to differences in

pressure at the top and bottom punches. Although the system is designed so that the sample is pressed from both ends, the pressure at the bottom may be distributed in part to the carbon black insulation under the bottom of the mold. Thus the carbide-graphite particles toward the top of the charge may be in more intimate contact and more susceptible to eutectic formation.

With materials having a carbide content of 70 vol% or greater, sample melting and the resulting extrusion and reaction with the mold is much more pronounced. This is due to the fact that at these high carbide concentrations more than 90 vol% of the sample would be liquid and little solid graphite would be available to retard loss of material. Figure 3 shows the eutectic structure with excess graphite which can occur. Thus, fabrication of NbC-C bodies have been conducted in the range 3100° to 3200°C so that such loss of material might be avoided.

Composites in the TaC-C system have been hot pressed at temperatures of 3200° to 3250°C. A closer approach to the eutectic temperature of 3450°C is restricted by practical limitations such as the low creep resistance of the graphite molds. This is reflected in changes in plunger lengths ranging from 10 to 20% depending on the pressing temperature.

III. EVALUATION OF PROPERTIES

A number of compositions ranging from 20 to 80 vol% carbide have been prepared in each of the two systems. These billets were sectioned into samples of both grain directions for evaluation. The initial examination involved density measurements, analysis for metal content and microstructural studies. Physical properties which have been determined include flexural strength, thermal expansion, high temperature compressive deformation, and limited data for tensile and compressive strengths.

A. Density

Density determinations were made by both precise measurements of dimensions and weight and also be water immersion techniques. In general, densities have ranged from 95 to 98% of theoretical. Care was taken to determine accurately the actual metal content in these evaluations. The analysis consisted of oxidizing the metal carbide-graphite under a stream of oxygen at 900°C to obtain the metal oxide while volatilizing the carbon component as CO and/or CO_2. Gravimetric analysis revealed the actual amounts of metal in the samples.

B. Flexural Strength

Much of the physical properties evaluation has been concerned with 4-point flexural strength measurements. These tests are relatively simple and sample configurations are fabricated easily. In view of the large number of compositions and systems which were investigated on our program, flexural strength determinations were used to give a rapid indication as to relative mechanical behavior.

1. Effect of Carbide Content: NbC-C

The data in Fig. 4 represents the highest strength composites observed for the NbC-C system with respect to composition. At 20 vol%, W/G strengths of about 15,000 psi and A/G strengths of about 4000 psi can be expected. At a carbide content of 86 vol%, strength in the weaker direction is close to 20,000 psi. The relationship of higher strengths with increased carbide contents appear to be linear for the W/G direction and curvilinear for the A/G direction. The anisotropy ratio drops from a value over 4 to 1.4 at 86 vol% NbC. This can be expected as the cubic, isotropic carbide becomes the dominant phase in the composites. As seen in microstructures for the 86 vol% NbC composite in Figs. 5 and 6, some directionality can be seen for the graphite

phase in the W/G direction. This orientation is, of course, not observed in the A/G direction.

Extrapolation of the curve to pure NbC would suggest a strength of about 28,000 psi. Preliminary tests conducted on a material prepared by hot pressing of stoichiometric amounts of niobium and carbon reveals this value to be valid. Higher values ranging from 36,000[4] to 54,000 psi[5] for pure NbC have been reported in the literature. It would appear that using our particular raw materials, i.e., 10μ niobium metal plus calcined petroleum coke, and our processing methods, we are obtaining bodies having somewhat low strengths. It is possible that with the use of finer particle size powders of metal or carbide or even a different carbon source, higher strength composites may be realized.

2. Effect of Temperature: NbC-C

It is in the area of high temperature performance that carbide-graphite composites take on significance. As shown in Fig. 7, all of the NbC-C composites were of higher strength at 2000°C than at room temperature. This is probably a contribution of the graphite phase which can be expected to be stronger at the higher temperatures. The peak in strength appears to be at 2000°C for the composites, with lower strengths at 2500°C where pure graphite usually peaks. It would appear that at 2500°C the high temperature plastic behavior of pure NbC begins to become a dominant force.

3. Effect of Carbide Content: TaC-C

An especially satisfying aspect of our studies has been the fabrication of strong TaC-C composites. Early work carried on at temperatures of 2800° to 3000°C had produced weak, friable bodies. However, raising the fabrication temperature to over 3200°C resulted in dense, well-bonded composites. The strength vs carbide content curves (Fig. 8) are similar to those for the

NbC-C system. The anisotropy ratio drops from a value of 5.6 at 20 vol% TaC to 1.5 at 80 vol%. Examination of the microstructure of the 80 vol% composite revealed strongly oriented graphite particles in a carbide matrix (Figs. 9 and 10).

The data point seen as 19,000 psi at 20 vol% was for a billet which was probably fabricated at temperature near 3400°C. This was the only TaC-C composite which reacted with the mold, and a coning effect previously described for NbC-C had also occurred. However, such high temperatures are extremely difficult to predict and control, so the majority of the bodies were fabricated in the range 3200° to 3250°C.

4. Effect of Temperature: TaC-C

As was the case with NbC-C bodies, all materials showed higher strengths at 2000°C (Fig. 11) and a decline in strength at 2500°C. At 2800°C, all of the NbC-C composites had exhibited strong plastic deformation and could not be stressed to failure. Although creep was also displayed by TaC-C bodies, it was considerably less and fracture points were obtained.

In both systems, it is interesting to note that even the high carbide materials in which the carbide is the dominant phase, showed increased strength at 2000°C. The 2000°C strength of pure TaC is listed at 17,000 psi by Shaffer[4] and also by Johansen.[6] This value is almost doubled by the 80 vol% TaC composite, and may be due to the small amounts of graphite acting as crack stoppers. There is also the possibility that some stresses brought on by difference in thermal expansion may actually act to strengthen the material at 2000°C. In Fig. 12 the varying amount of plastic deformation in flexural strength tests at elevated temperatures can be seen.

C. Coefficient of Thermal Expansion

Thermal expansion behavior has been examined at temperatures up to 2300°C. Figure 13 shows this property as a function

of carbide content in the TaC-C system. The trend toward isotropic behavior as the carbide becomes the dominant force is quite evident. Figure 14, which reveals the behavior of the NbC-C system is quite similar. In both systems, essentially isotropic behavior is indicated at a carbide content of about 70 vol%. The values observed for the 86 vol% NbC and 80 vol% TaC samples are quite close to those for the pure carbides.

In the CTE evaluations, permanent dimensional changes were seen to occur for graphite matrix materials. These changes were an increase of up to 1% in the A/G direction and a decrease in the W/G direction of about .5%. Such changes were inversely related to carbide content and were not observed in the high carbide materials. These are probably due to a relaxation of stresses imparted to the composite during hot pressing.

D. High Temperature Creep

A series of experiments were conducted to determine compressive deformation under the conditions 2700°C/2000 psi/ 30 min. Under these relatively moderate conditions, changes were all quite limited as shown in Fig. 15. The curves indicate two trends:

1) Creep behavior is related to increasing carbide content.
2) TaC-C composites are more resistant to creep than NbC-C bodies.

The superior performance of TaC-C bodies as compared to that for NbC-C might be expected in consideration of the melting points of 4000°C for TaC and 3500°C for NbC.

Recently, experiments were conducted in flexure at 2400°C and 8000 psi in an attempt to magnify changes for clarification of compositional effects. The trend toward greater deformation with increasing carbide content appears to hold. An interesting result has been that under these severe conditions, 80 vol% NbC-C samples exhibit more than 10 times the creep shown by an equivalent TaC-C specimen.

E. Other Properties

Other properties which have been determined include compressive and tensile strengths at room temperature. In general, compressive strength values for graphite matrix materials were 2 to 2.5 times higher than flexural strengths. These ratios increase with higher carbide materials to values of 4 to 6. The highest strengths which have been observed are 190,000 psi for 86 vol% NbC-C and 120,000 psi for 80 vol% TaC-C.

Tensile tests have been conducted with pin-type dogbone specimens as shown in Fig. 16. Strength values which have been determined for high carbide content materials are:

1) 73 vol% NbC - 18,610 psi
2) 84 vol% NbC - 21,200 psi
3) 80 vol% TaC - 19,550 psi

These values are quite high in light of flexural data, the ratio being about 1.2 to 1.4 for flexural to tensile. The ratios observed for graphite varies from about 1.4 to 2.0,[7] and for carbides, 2 or higher.[8]

F. Effect of Heat Treatment

As pointed out earlier, dimensional changes have been seen to occur when samples were heat treated at elevated temperatures. Another effect which has been observed is improvement in strength for poorly bonded NbC matrix composites.

The data in Table I present changes in resistivity and flexural strength for composites containing 73 vol% NbC. Permanent decreases in resistivity occurred for all samples; they were particularly pronounced for some of the C3-80Nb specimens. The flexural strengths of the heat-treated samples confirm the improved bonding suggested by the changes in electrical resistivity.

These particular annealing conditions failed to change the properties of graphite matrix composites and TaC-C samples. Thus, it would appear that improvement in strength occurs due to improved bonding by sintering rather than by relief of stresses. The heat treatment step subsequent to hot pressing can be quite important in obtaining sound materials and of equal importance is the dimensional stability which would be achieved prior to actual use at elevated temperatures.

IV. SUMMARY

In summary, our work with hot pressed TaC-C and NbC-C composites has suggested optimum fabrication parameters and also mechanical behavior which may be expected. The beneficial effect of higher processing temperatures in obtaining dense, well-bonded composites is quite clear. The limiting factors are excessive loss of material through extrusion and reaction with the mold.

Certain trends exist for mechanical behavior with increasing carbide content. They are as follows:

1) Higher strengths
2) Isotropic behavior
3) Susceptibility to high temperature creep

In comparison of systems, TaC-C composites are significantly more creep resistant than NbC-C bodies.

Our future work will be concerned with further characterization of mechanical and thermal properties. Additional studies will also consider a closer look at the effect of raw materials and fabrication procedures in selected compositions. Focusing of investigations into more specific areas is a logical follow-on to the fairly broad studies conducted to date.

V. ACKNOWLEDGEMENTS

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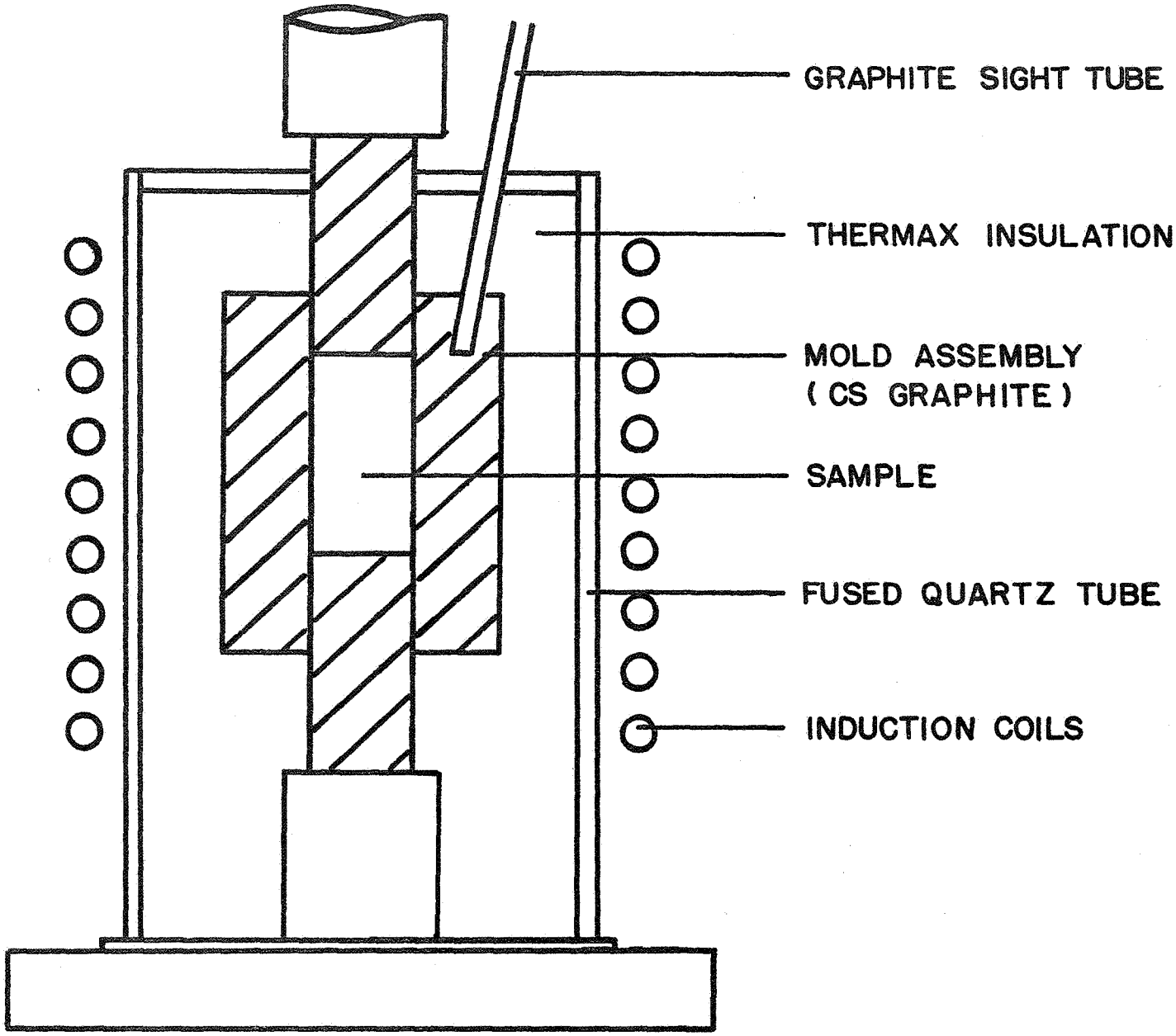

Fig. 1 - HOT PRESSING APPARATUS

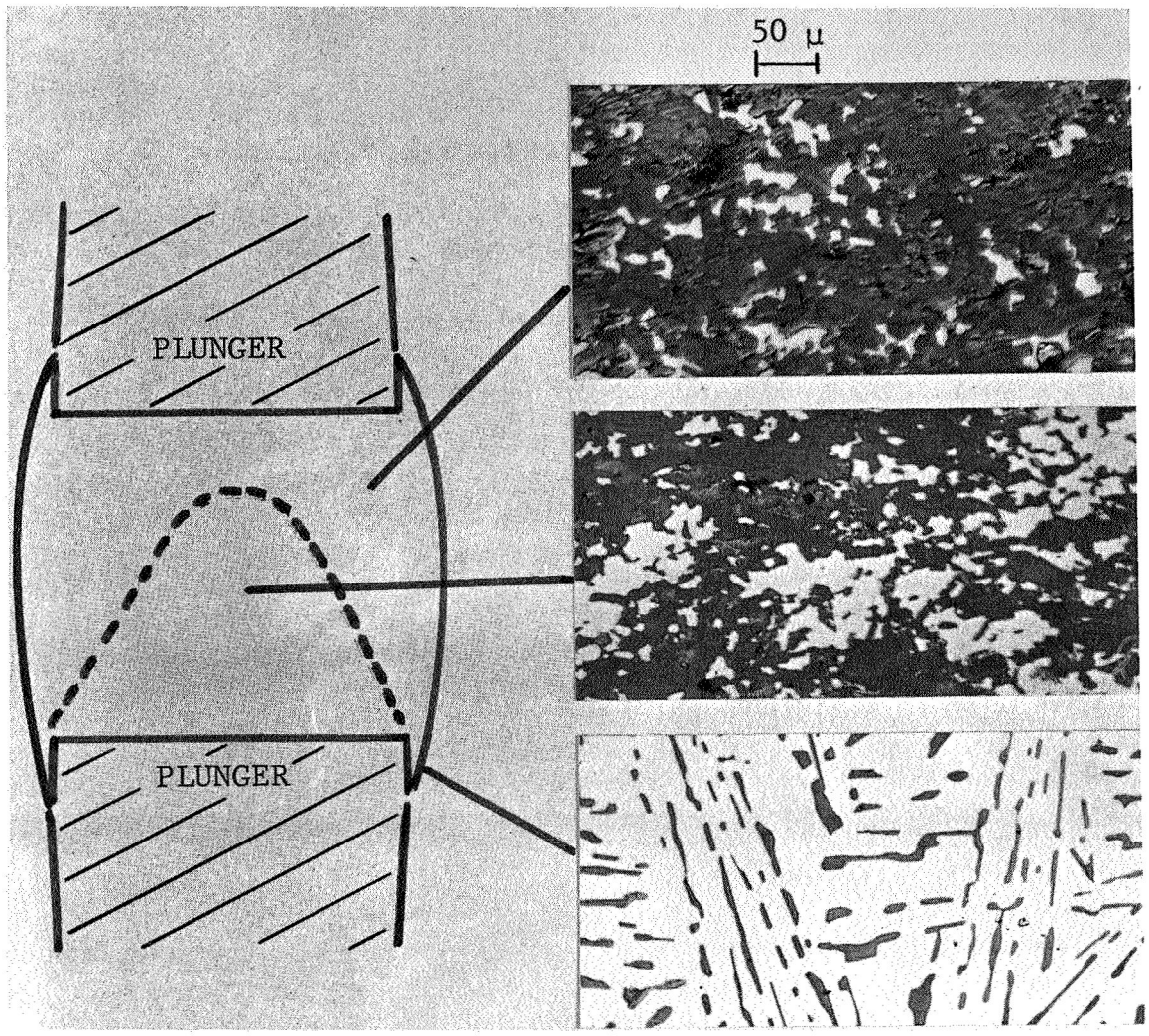

Fig. 2 - "CONING" EFFECT IN Nb-C COMPOSITE SHOWING HETEROGENEITY IN CARBIDE CONTENT AND FORMATION OF EUTECTIC STRUCTURE

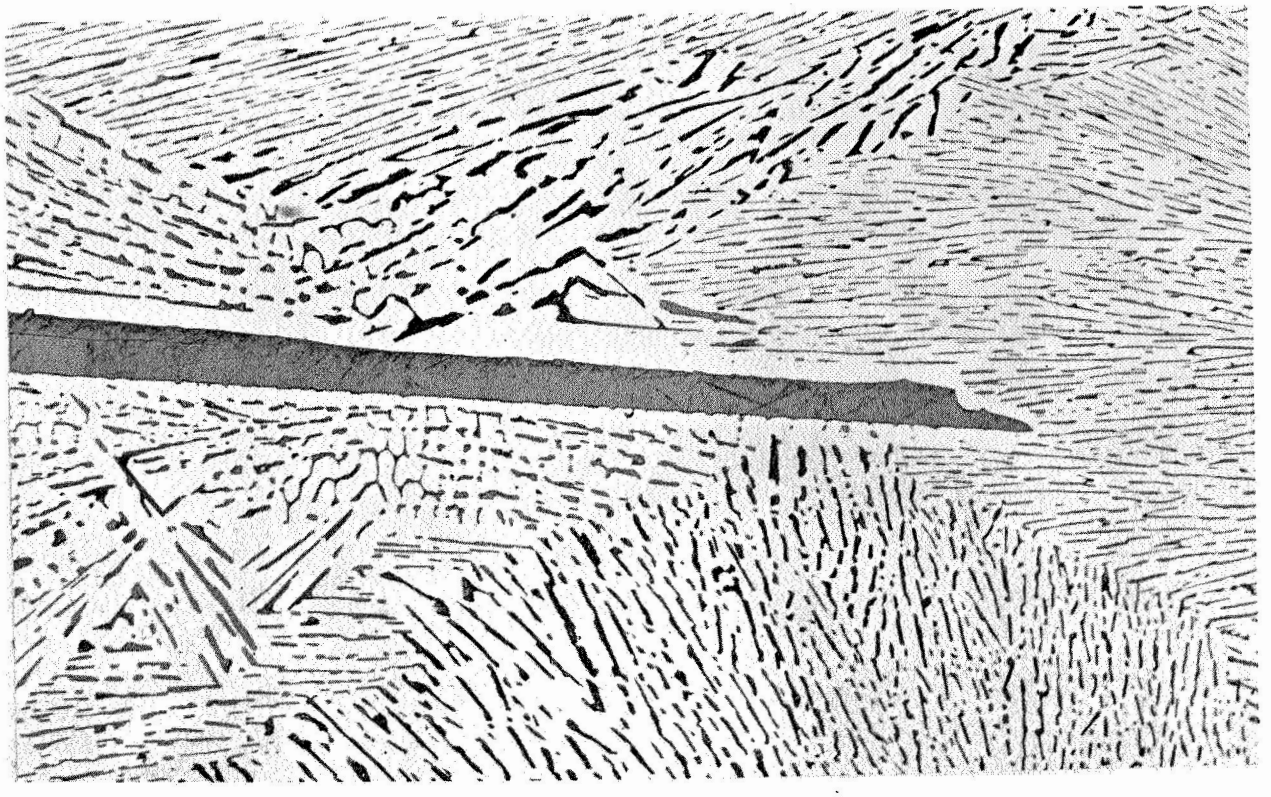

Fig. 3 - MICROSTRUCTURE OF ZONE ON RECRYSTALLIZED MELT IN 73 VOL% NbC-C COMPOSITE SHOWING EUTECTIC STRUCTURE (200X)

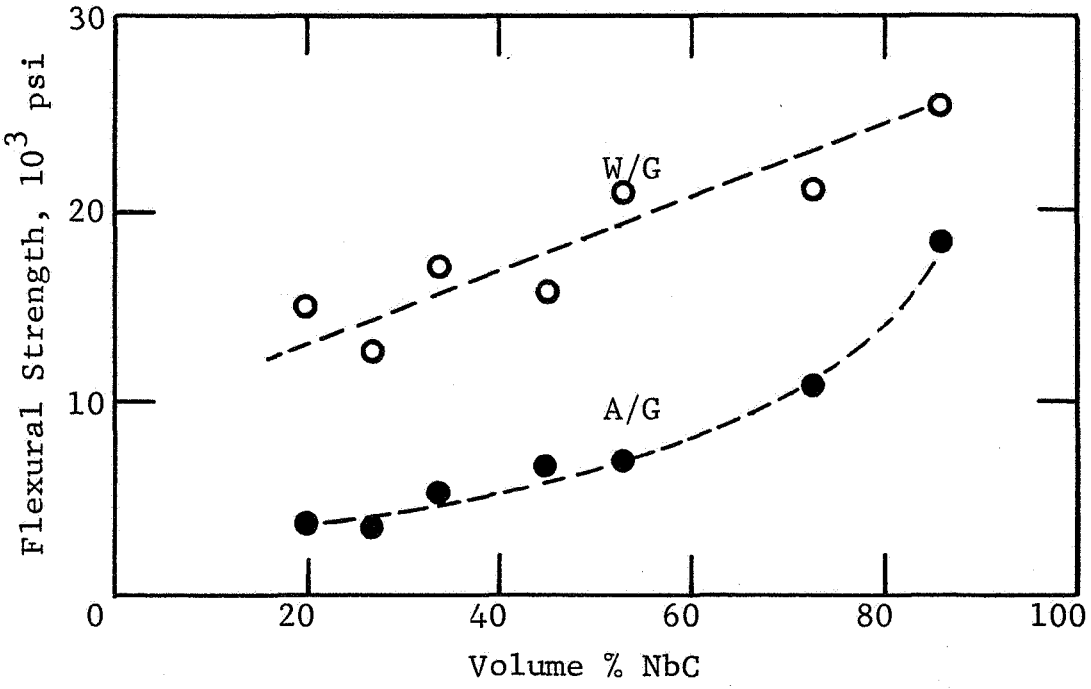

Fig. 4 - FLEXURAL STRENGTH VS COMPOSITION FOR NbC-C COMPOSITES

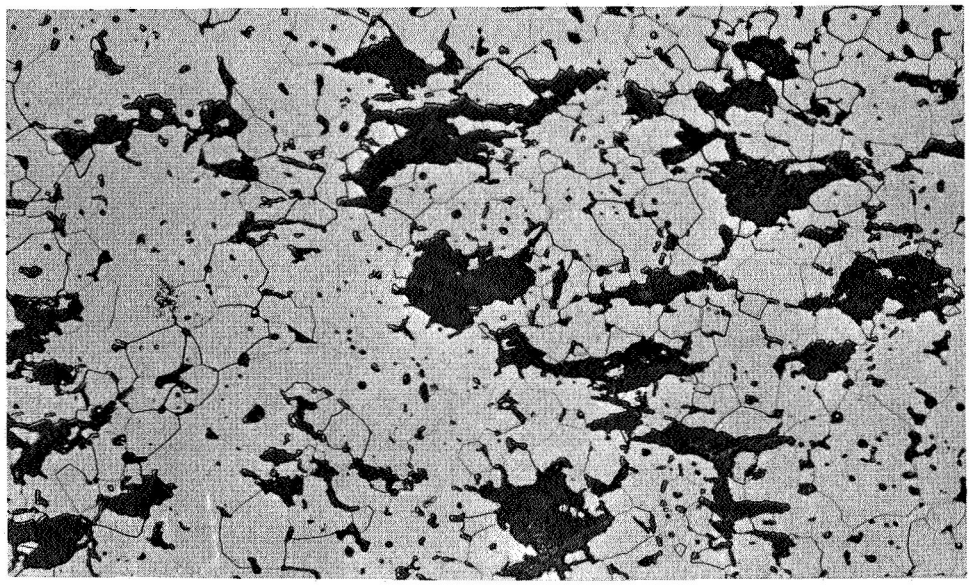

Fig. 5 - MICROSTRUCTURE OF 73 VOL% NbC-C COMPOSITE IN W/G DIRECTION SHOWING OREINTATION OF GRAPHITE PHASE (320X)

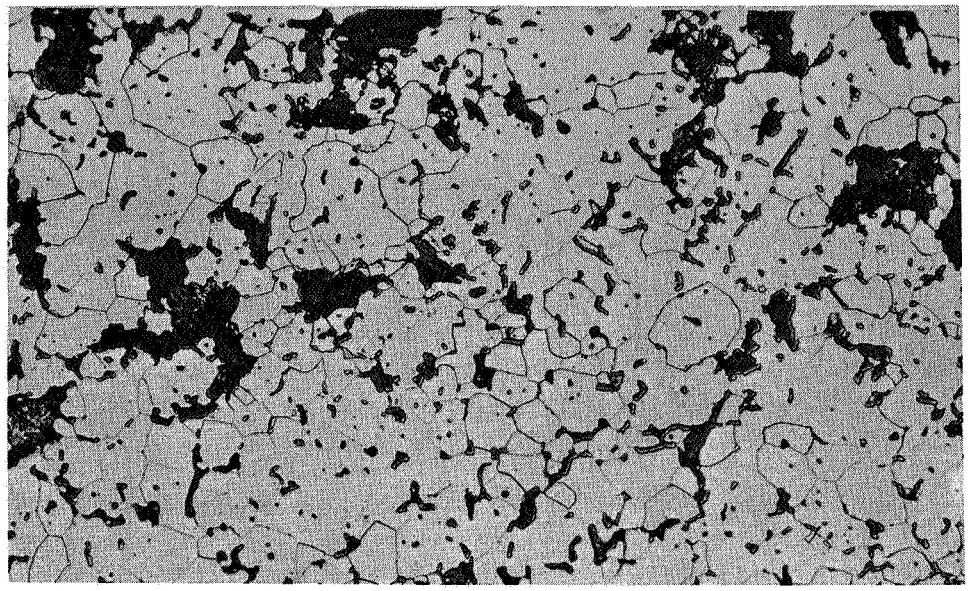

Fig. 6 - MICROSTRUCTURE OF 73 VOL% NbC-C COMPOSITE IN A/G DIRECTION SHOWING LACK OF ORIENTATION OF BOTH PHASES (320X)

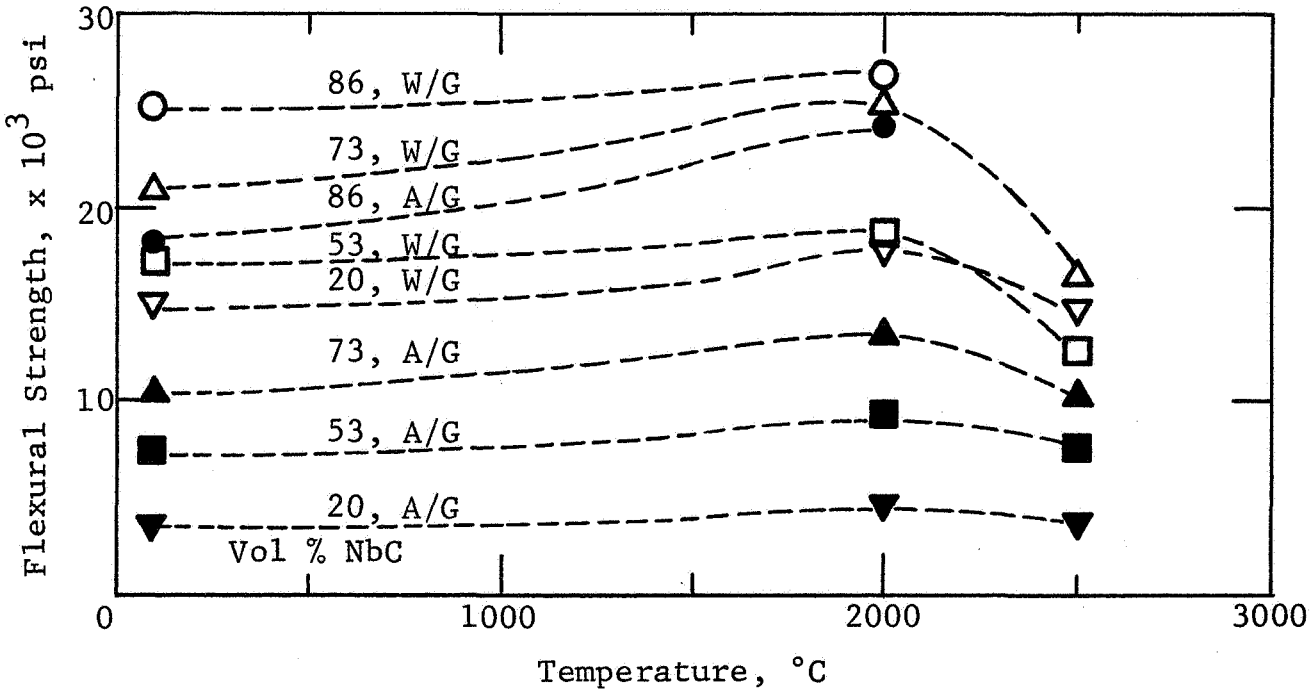

Fig. 7 - FLEXURAL STRENGTH VS TEMPERATURE FOR NbC-C COMPOSITES

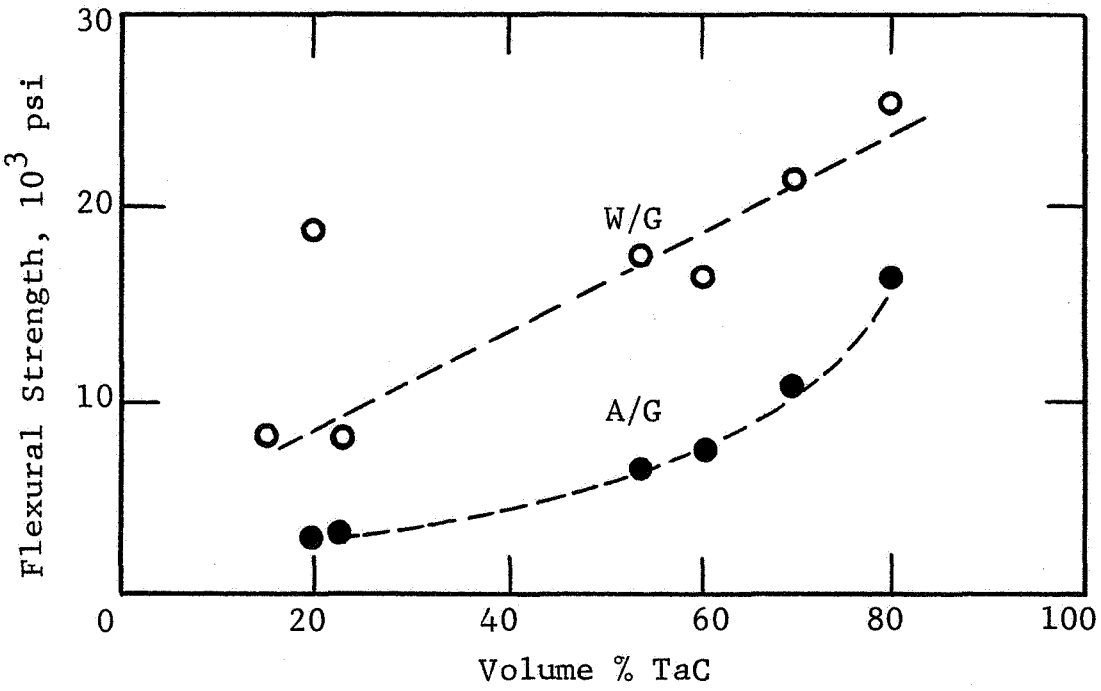

Fig. 8 - FLEXURAL STRENGTH VS COMPOSITION FOR TaC-C COMPOSITES

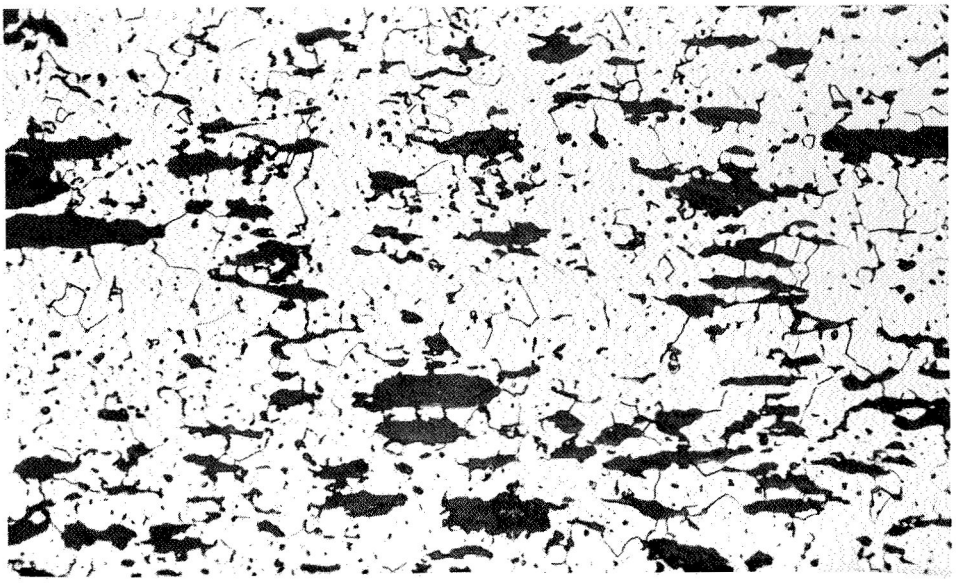

Fig. 9 - MICROSTRUCTURE OF 90 VOL% TaC-C COMPOSITE IN W/G DIRECTION SHOWING ORIENTATION OF GRAPHITE PHASE (320X)

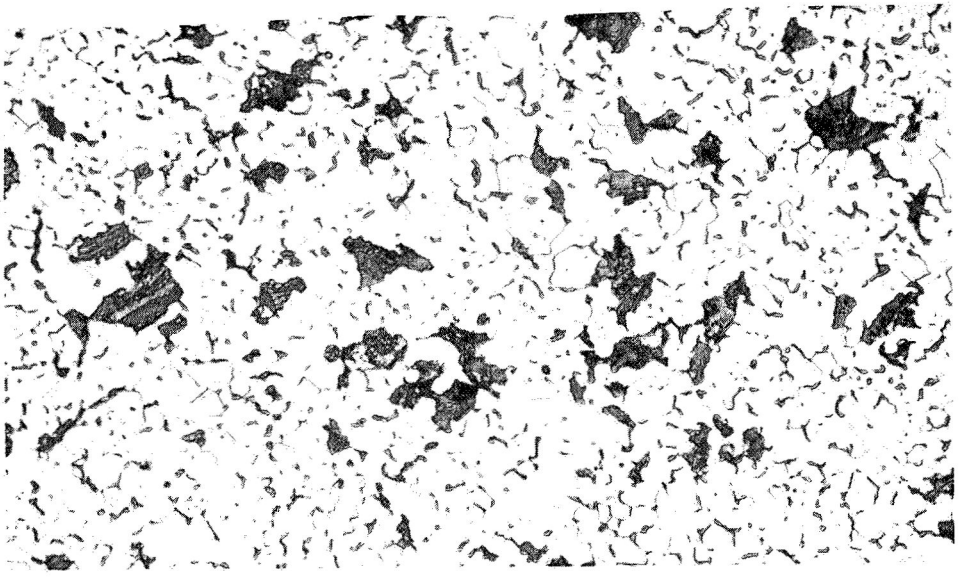

Fig. 10 - MICROSTRUCTURE OF 90 VOL% TaC-C COMPOSITE IN A/G DIRECTION SHOWING LACK OF ORIENTATION OF BOTH PHASES (320X)

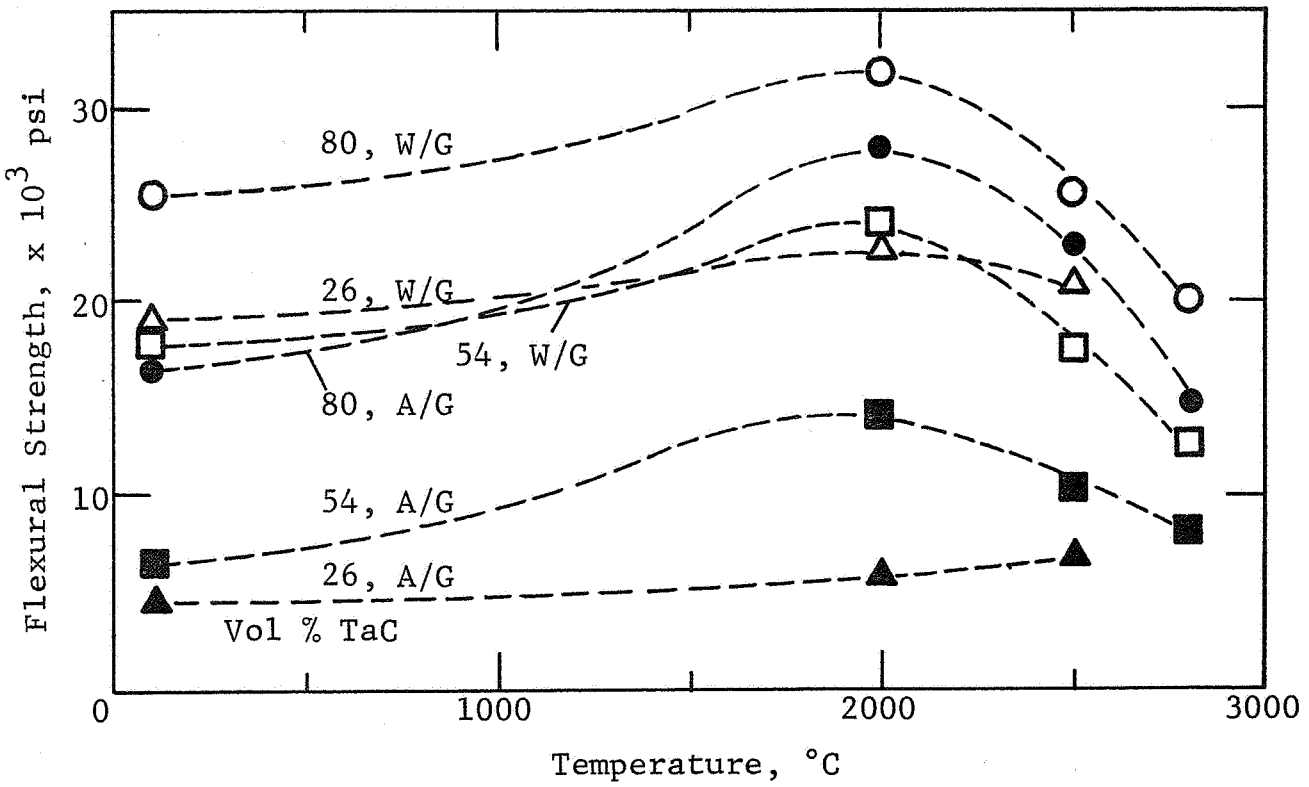

Fig. 11 - FLEXURAL STRENGTH VS TEMPERATURE FOR TaC-C COMPOSITES

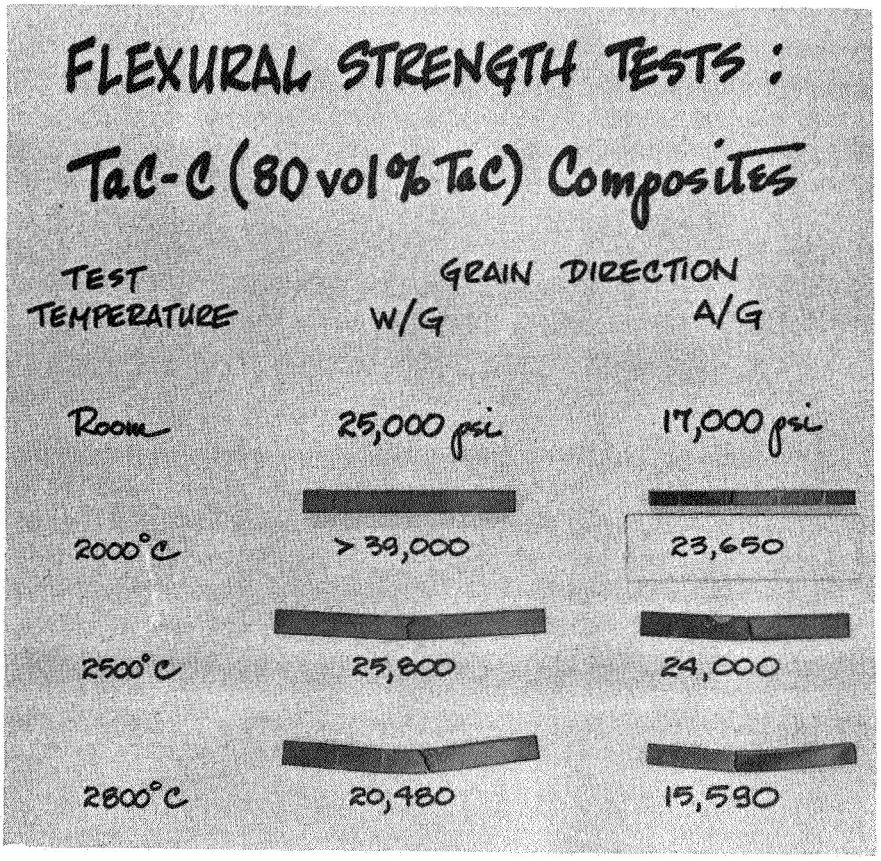

Fig. 12 - FLEXURAL STRENGTH TEST SPECIMENS SHOWING EXTENT OF PLASTIC DEFORMATION OF VARIOUS TEMPERATURES

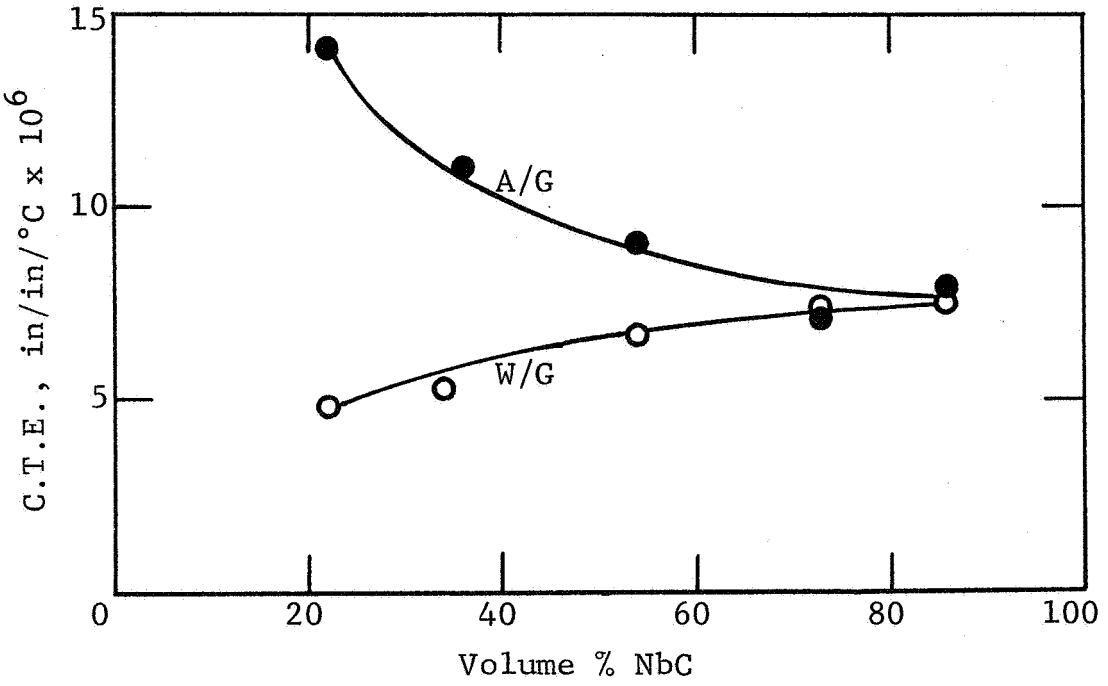

Fig. 14 - COEFFICIENT OF THERMAL EXPANSION VS COMPOSITION FOR NbC-C COMPOSITES (RT - 2300°C)

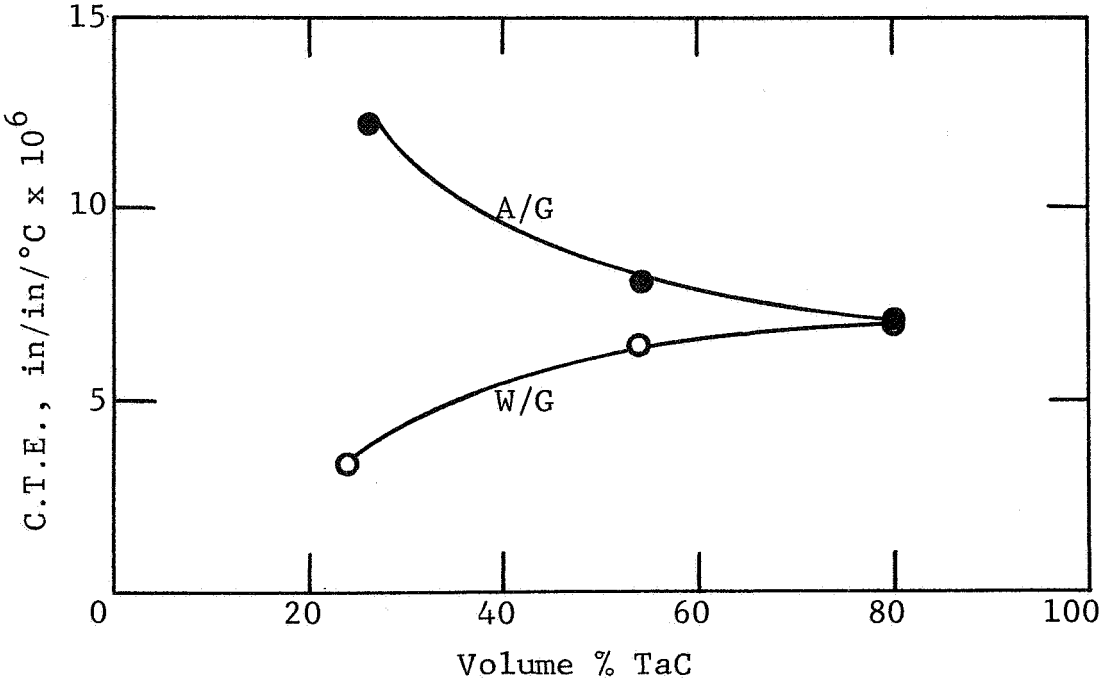

Fig. 13 - COEFFICIENT OF THERMAL EXPANSION VS COMPOSITION FOR TaC-C COMPOSITES (RT - 2300°C)

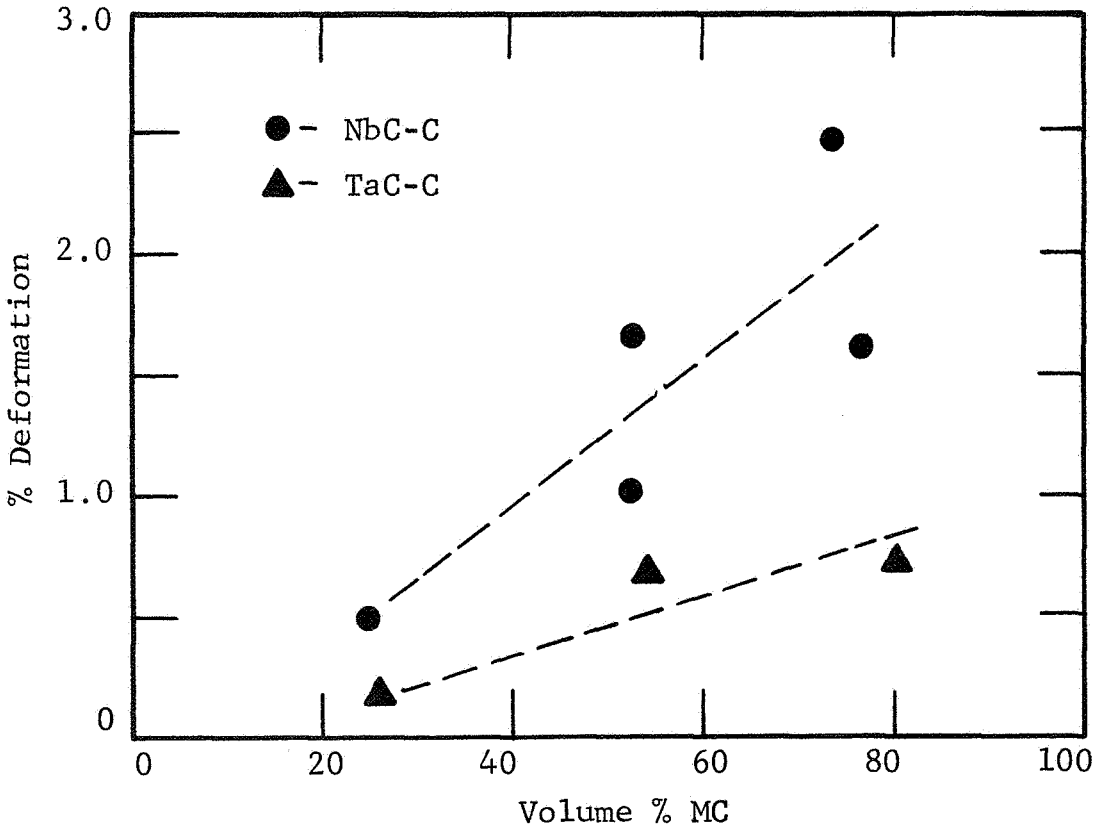

Fig. 15 - COMPRESSIVE DEFORMATION VS COMPOSITION FOR NbC-C and TaC-C COMPOSITES (2700°C/2000 psi/30 min)

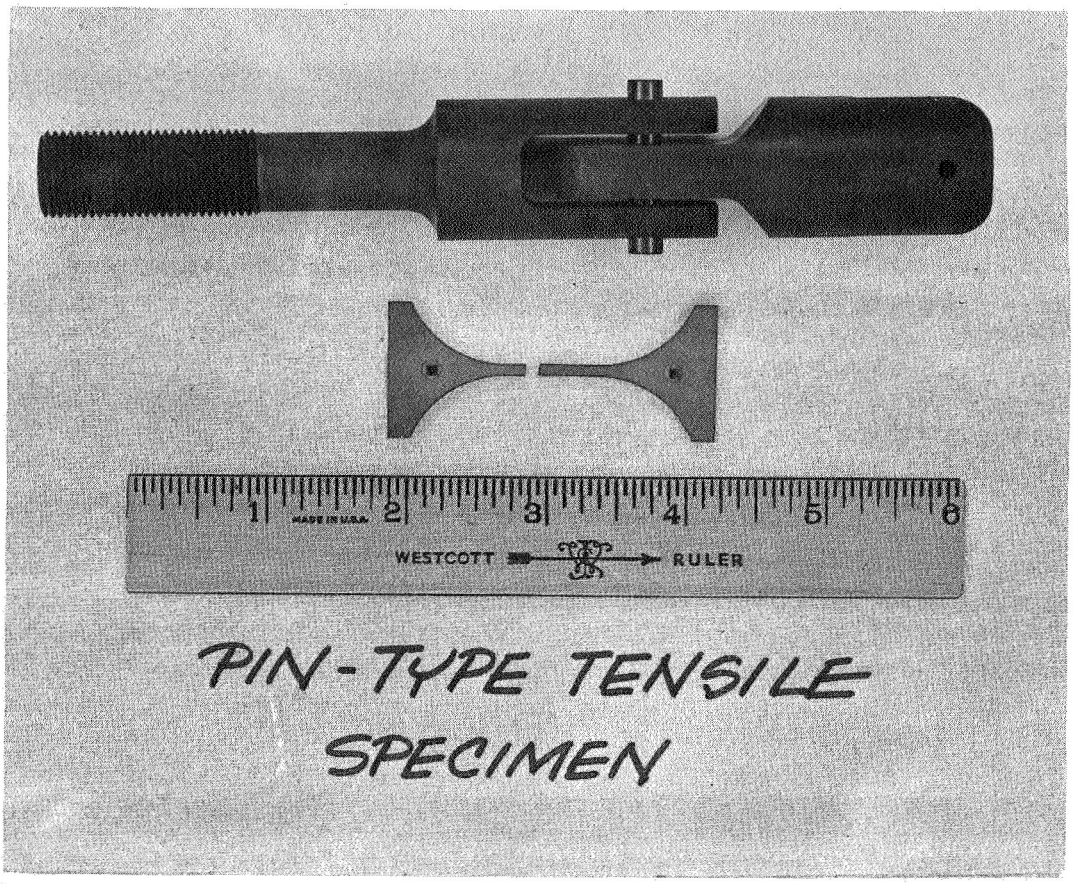

Fig. 16 - SPECIMEN CONFIGURATION
FOR TENSILE TESTING

Table I

EFFECT OF HEAT TREATMENT ON MECHANICAL
AND ELECTRICAL PROPERTIES
OF SELECTED 73 vol% NbC-C SAMPLES

Sample No.	Grain Direc.	As Pressed		2500°C/1 Hour	
		Flexural Strength, psi	Elec. Resis. μΩ-cm	Flexural Strength, psi	Elec. Resis. μΩ-cm
5A	W/G	6,660*	52.1	16,530	45.6
5C	W/G		56.3	16,630	48.2
1C	W/G		232	12,130	45.5
1A	A/G	4,010*	82.6	12,830	61.1
4A	A/G		284	7,950	63.0
2B	A/G		160	10,260	53.1

* Averages for 4 or more samples